INDUCED REACTIONS WITHIN THE PEROXY COMPOUNDS. II

Effect of Foreign Substances on the Induced Reaction Occurring in the $H_2O_2-H_2S_2O_8-KMnO_4$ System

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(Received November 15, 1962)

The effect of foreign ions on the induced reaction occurring in the $H_2O_2-H_2S_2O_8-KMnO_4$ (and $-Ce(SO_4)_2$, resp.) system was studied and found that the induced error is increased by silver(I)-, copper(II)- and iron (III)-ions, while decreased by alkali-, alkali earth metal ions, tin (IV), lead (II), chromium (III), nickel (II), cobalt (II), cerium (III)-, molybdate and tungstate-ion and especially by halide ions.

Preliminary observations [1] clearly showed that the induced reaction occurring during oxidimetric titration of hydrogen peroxide in presence of peroxydisulphate may be considerably influenced by foreign substances. The influence may be either positive or negative. In this paper we compile the results of detailed study of the effect of foreign substances on the induced reaction.

Experimental

Substances used for the measurements were all chemicals of c. p. degree. Some substances needed to be purified in spite of the c. p. qualification. Besides the customary methods if the quality of the substances made this possible, d'ANS and MATTER's [2] method was applied, too.

In a previous paper [3] it was described, how the induced reaction in the $H_2O_2-H_2S_2O_8-KMnO_4$ system depends on the experimental conditions. The knowledge of this made possible to choose such experimental conditions for the study of the foreign substances which, on the one hand assured quite a considerable induced error and satisfactory reproducibility on the other. Measurements were performed in the following manner: 5 ml 2% nitric acid and 10 ml 0,1 N peroxydisulphate and salt solutions to be investigated were measured into an Erlenmeyer flask of 250 ml volume and filled up with water to 60 ml initial volume. Immediately before titration 10 ml 0,1 N hydrogen peroxide was added and by vigorous shaking and at constant delivery rate hydrogen peroxide was titrated with permanganate. At each measurement the time of titration was 120 ± 10 sec. After the titration of hydrogen peroxide the amount of peroxydisulphate was determined, too. The applied method was described earlier [4]. According to the measurements the $H_2S_2O_8$-error agreed in each case with the H_2O_2-error, therefore the presentation of the peroxydisulphate data is not necessary.

Experimental results

According to the measurements alkali metal ions slightly decrease the induced error (Table I).

Table I

	Conc. mole/l	Taken 0,1 N H_2O_2	Found ml	ΔH_2O_2 ml
Li_2SO_4	0,00	10,10	9,29	0,81
	0,075	10,10	9,29	0,81
	0,15	10,10	9,30	0,80
	0,45	10,10	9,35	0,75
	0,75	10,10	9,43	0,67
Na_2SO_4	0,00	10,09	9,25	0,84
	0,055	10,09	9,27	0,82
	0,110	10,09	9,28	0,81
	0,330	10,09	9,33	0,76
	0,550	10,09	9,38	0,71
K_2SO_4	0,00	9,97	9,12	0,85
	0,048	9,97	9,12	0,85
	0,096	9,97	9,15	0,82
	0,288	9,97	9,24	0,73
	0,480	9,97	9,26	0,71
$(H_4N)_2SO_4$	0,00	10,05	9,20	0,85
	0,063	10,05	9,39	0,66
	0,126	10,05	9,44	0,61
	0,378	10,05	9,57	0,48
	0,630	10,05	9,76	0,29

Alkali earth metal ions bring about the decrease of the induced reaction (Table II).

Table II

	Conc. mole/l	Taken 0,1 N H_2O_2	Found ml	ΔH_2O_2 ml
$Ca(NO_3)_2$	0,00	9,25	8,55	0,70
	0,035	9,25	8,55	0,70
	0,070	9,25	8,70	0,55
	0,210	9,25	8,75	0,50
	0,350	9,25	8,80	0,45
$Sr(NO_3)_2$	0,00	10,05	9,30	0,75
	0,038	10,05	9,40	0,65
	0,076	10,05	9,50	0,55
	0,228	10,05	9,65	0,40
	0,380	10,05	9,70	0,35
$Ba(NO_3)_2$	0,00	9,25	8,45	0,80
	0,030	9,25	8,60	0,65
	0,060	9,25	8,70	0,55
	0,180	9,25	8,75	0,50
	0,30	9,25	8,80	0,45

Elements of the zinc group increased the induced error even after the most various purifications (Table III).

Table III

	Conc. mole/l	Taken 0,1 N H_2O_2	Found ml	ΔH_2O_2 ml
$BeSO_4$	0,00	10,07	9,35	0,72
	0,0235	10,07	9,10	0,97
	0,0470	10,07	8,90	1,17
	0,0705	10,07	8,60	1,47
	0,0940	10,07	8,25	1,82
	0,2820	10,07	8,05	2,02
$Mg(NO_3)_2$	0,00	10,10	9,50	0,60
	0,030	10,10	9,65	0,45
	0,060	10,10	9,70	0,40
	0,180	10,10	9,75	0,35
	0,300	10,10	9,85	0,25
$ZnSO_4$	0,00	10,10	9,35	0,75
(Chinoin c. p.)	0,028	10,10	8,65	1,45
	0,056	10,10	8,35	1,75
	0,168	10,10	8,15	1,95
	0,280	10,10	7,90	2,20
$ZnSO_4$	0,00	10,10	9,35	0,75
(Merck c. p.)	0,028	10,10	9,15	0,95
	0,056	10,10	9,00	1,10
	0,168	10,10	8,85	1,25
	0,280	10,10	8,70	1,40
$CdSO_4$	0,00	10,23	9,57	0,66
	0,037	10,23	9,55	0,68
	0,074	10,23	9,53	0,70
	0,222	10,23	9,48	0,75
	0,370	10,23	9,43	0,80
$Hg(NO_3)_2$	0,00	10,23	9,56	0,67
	0,025	10,23	9,45	0,78
	0,050	10,23	9,40	0,83
	0,150	10,23	9,37	0,86
	0,250	10,23	9,32	0,91

Boric acid, aluminium(III)-, thallium(III)-, cerium(III)-sulphate scarcely influenced the induced reaction or decreased it only to a small extent (Table IV).

Table IV

	Conc. mole/l	Taken 0,1 N H_2O_2	Found ml	ΔH_2O_2 ml
H_3BO_3	0,00	10,05	9,37	0,68
	0,133	10,05	9,40	0,65
	0,266	10,05	9,43	0,62
	0,798	10,05	9,45	0,60
	1,330	10,05	9,50	0,55

Table IV

	Conc. mole/l	Taken 0,1 N H_2O_2	Found ml	ΔH_2O_2 ml
$Al_2(SO_4)_3$	0,00	9,82	8,97	0,85
	0,023	9,82	8,98	0,84
	0,046	9,82	8,97	0,85
	0,138	9,82	8,97	0,85
	0,230	9,82	8,97	0,85
$Tl_2(SO_4)_3$	0,00	10,05	9,35	0,70
	0,010	10,05	9,37	0,68
	0,020	10,05	9,37	0,68
	0,060	10,05	9,37	0,68
	0,100	10,05	9,40	0,65
$Ce_2(SO_4)_3$	0,00	10,08	9,40	0,68
	0,010	10,08	9,43	0,65
	0,020	10,08	9,45	0,63
	0,040	10,08	9,48	0,60
	0,050	10,08	9,52	0,56
	0,100	10,08	9,55	0,53
	0,250	10,08	9,75	0,33

Tin(IV)- and lead (II)-nitrate, sodium metasilicate decrease the induced error. Arsenate ions, bismuth(III)-nitrate similarly lead to the decrease of the error (Table V).

Table V

	Conc. mole/l	Taken 0,1 N H_2O_2	Found ml	ΔH_2O_2 ml
$Sn(NO_3)_4$	0,00	10,05	9,33	0,72
	0,021	10,05	9,45	0,60
	0,042	10,05	9,60	0,45
	0,126	10,05	9,75	0,30
	0,210	10,05	9,87	0,18
$Pb(NO_3)_2$	0,00	10,05	9,35	0,70
	0,025	10,05	9,55	0,50
	0,050	10,05	9,68	0,37
	0,150	10,05	9,76	0,29
	0,250	10,05	9,85	0,20
Na_2SiO_3	0,00.	10,07	9,35	0,72
	0,029	10,07	9,45	0,62
	0,058	10,07	9,65	0,42
	0,174	10,07	9,80	0,27
	0,290	10,07	9,95	0,12
Na_2HAsO_4	0,00	10,05	9,35	0,70
	0,026	10,05	9,45	0,60
	0,052	10,05	9,50	0,55
	0,156	10,05	9,65	0,40
	0,260	10,05	9,70	0,35
$Bi(NO_3)_3$	0,00	10,05	9,30	0,75
	0,0167	10,05	9,40	0,65
	0,0334	10,05	9,50	0,55
	0,1002	10,05	9,57	0,48
	0,1670	10,05	9,63	0,42

Sulphate and selenate ions have error-decreasing effect. Chromium(III)-sulphate, molybdate, tungstate and vanadate-ions similarly cause the decrease of the error (Table VI).

Table VI

	Conc. mole/l	Taken 0,1 N H_2O_2	Found ml.	ΔH_2O_2 ml
Na_2SO_4	0,00	10,09	9,25	0,84
	0,055	10,09	9,27	0,82
	0,110	10,09	9,28	0,81
	0,330	10,09	9,33	0,76
	0,550	10,09	9,38	0,71
Na_2SeO_4	0,00	9,97	9,25	0,72
	0,044	9,97	9,27	0,70
	0,088	9,97	9,35	0,62
	0,264	9,97	9,45	0,52
	0,440	9,97	9,56	0,41
$Cr_2(SO_4)_3$	0,00	10,10	9,35	0,75
	0,021	10,10	9,40	0,70
	0,042	10,10	9,47	0,63
	0,126	10,10	9,54	0,56
	0,210	10,10	9,63	0,47
Na_2MoO_4	0,00	9,93	9,25	0,68
	0,034	9,93	9,70	0,23
	0,068	9,93	9,78	0,15
	0,204	9,93	9,84	0,09
	0,340	9,93	9,96	0,07
Na_2WO_4	0,00	10,06	9,35	0,71
	0,028	10,06	9,45	0,61
	0,056	10,06	9,57	0,49
	0,168	10,06	9,63	0,43
	0,280	10,06	9,68	0,38
$NaVO_3$	0,00	9,97	9,25	0,72
	0,034	9,97	9,30	0,67
	0,068	9,97	9,45	0,52
	0,102	9,97	9,57	0,40
	0,136	9,97	9,65	0,32
	0,272	9,97	9,75	0,22

Manganese(II)-ions, especially in greater quantity, exert strong error-decreasing effect. Iron(III)-ions, on the contrary, increase the error. The effect of iron(III)-ions is especially considerable when containing small quantity of iron(II)-ions, too (Table VII).

Table VII

	Conc. mole/l	Taken 0.1 N H_2O_2	Found ml	ΔH_2O_2 ml
$Mn(NO_3)_2$	0,00	9,85	8,95	0,90
	0,033	9,85	9,10	0,75
	0,066	9,85	9,25	0,60
	0,198	9,85	9,30	0,55
	0,330	9,85	9,55	0,30
$MnSO_4$	0,00	10,10	9,35	0,75
	0,036	10,10	9,70	0,40
	0,072	10,10	9,85	0,25
	0,216	10,10	9,90	0,20
	0,360	10,10	—	—
$Fe(SO_4)_3$	0,00	10,15	9,45	0,70
	0,010	10,15	9,40	0,75
	0,020	10,15	9,35	0,80
	0,040	10,15	9,20	0,95
	0,060	10,15	9,13	1,02
	0,080	10,15	9,02	1,13
	0,120	10,15	8,90	1,25
	0,160	10,15	8,75	1,40
60% $Fe_2(SO_4)_3$ + 40% $FeSO_4$	0,00	10,10	9,35	0,75
	0,003	10,10	7,75	2,35
	0,0060	10,10	6,25	3,85
	0,012	10,10	4,05	6,05
	0,018	10,10	1,70	8,40
	0,0240	10,10	1,08	9,02
	0,030	10,10	2,00	8,10
	0,063	10,10	5,82	4,28
	0,160	10,10	7,25	2,85

The effect of iron-ions bound in a complex is opposed to that of aquo-metal ions. *E. g.* iron(II)-tri-o-phenantrolin (ferroin) and iron(III)-hexacyanide complexes considerably decrease the induced error (Table VIII).

Table VIII

	Drop	Taken 0,1 N H_2O_2	Found ml	ΔH_2O_2 ml
Ferroin	0	10,07	9,35	0,72
	1	10,07	9,80	0,27
	3	10,07	10,00	0,07
	5	10,07	10,05	0,02
	Conc. mole/l			
$K_3[Fe(CN)_6]$	0,00	10,10	9,35	0,75
	0,025	10,10	9,40	0,70
	0,050	10,10	9,47	0,63
	0,100	10,10	9,52	0,58
	0,250	10,10	9,56	0,54

An interesting effect can be observed in presence of osmium tetroxide. Whilst the H_2O_2-error is strongly increased, the $H_2S_2O_8$-error decreased. Further investigations indicated clearly (it will be described in a subsequent paper) that osmic acid causes a considerable induced change even in absence of peroxydisulphate. Therefore, disregarding the H_2O_2-error increasing effect, it can be stated that osmium tetroxide inhibits the induced reaction occurring in the $H_2O_2-H_2S_2O_8$ system (Table IX).

Table IX

0,01 M OsO_4 drop	Taken 0,1 N H_2O_2	Fond ml	Δ H_2O_2 ml
0	10,10	9,35	0,75
1	10,10	7,95	2,15
2	10,10	7,35	2,75
4	10,10	6,95	3,15
6	10,10	6,55	3,55
8	10,10	6,25	3,85
10	10,10	5,95	4,15

0,01 N OsO_4 drop	Taken 0,1 N H_2O_2	Found ml	Δ H_2O_2 ml	$H_2S_2O_8$ ml	*Found 0,1 N H_2O_2 ml	*Δ H_2O_2 ml
0	10,10	9,40	0,70	0,65	10,10	—
2	10,10	7,50	2,60	0,35	7,93	2,17
4	10,10	6,75	3,25	0,18	7,01	3,09
6	10,10	6,45	3,65	0,10	6,70	3,40
8	10,10	6,20	3,90	0,05	6,25	3,85

* Data obtained in absence of $H_2S_2O_8$.

Cobalt(II), nickel(II)-ions decrease the induced error. Uranyl ions exert similar effect. On the contrary, copper(II) and silver(I) ions increase the induced error (Table X). The effect of copper(II) ions will be discussed in the following paper.

From among halide ions fluoride increases the error and on the contrary, chloride, bromide and ionide ions inhibit the induced reaction (Table XI).

Table X

	Conc. mole/l	Taken 0,1 N H_2O_2	Found ml	Δ H_2O_2 ml
$CoSO_4$	0,00	10,10	9,35	0,75
	0,0296	10,10	9,43	0,67
	0,0592	10,10	9,47	0,63
	0,1776	10,10	9,55	0,55
	0,2960	10,10	9,63	0,47
$Ni(NO_3)_2$	0,00	10,15	9,35	0,80
	0,026	10,15	9,40	0,75
	0,052	10,15	9,45	0,70
	0,162	10,15	9,55	0,62
	0,260	10,15	9,60	0,55

Table X

	Conc. mole/l	Taken 0,1 N H_2O_2	Found ml	ΔH_2O_2 ml
$UO_2(NO_3)_2$	0,00	9,93	9,25	0,68
	0,008	9,93	9,75	0,18
	0,016	9,93	9,80	0,13
	0,032	9,93	9,86	0,07
	0,064	9,93	9,90	0,03
$CuSO_4$	0,00	10,15	9,35	0,70
	0,000066	10,15	4,90	5,25
	0,00066	10,15	4,55	5,60
	0,0033	10,15	4,25	5,90
	0,0066	10,15	4,00	6,15
	0,0165	10,15	3,78	6,37
	0,033	10,15	4,70	5,45
	0,066	10,15	5,20	4,95
	0,198	10,15	6,20	3,95
	0,330	10,15	7,80	2,35
$AgNO_3$	0,00	9,76	9,05	0,71
	0,000096	9,76	8,75	1,01
	0,00096	9,76	8,35	1,41
	0,0096	9,76	7,95	1,81
	0,048	9,76	7,50	2,26
	0,096	9,76	6,40	3,36
	0,288	9,76	4,25	5,51
	0,480	9,76	3,25	6,51

Table XI

	Conc. mole/l	Taken 0,1 N H_2O_2	Found ml	ΔH_2O_2 ml
NaF	0,00	10,06	9,41	0,65
	0,0015	10,06	9,39	0,67
	0,0039	10,06	9,37	0,69
	0,0078	10,06	9,33	0,73
	0,0234	10,06	9,10	0,96
	0,039	10,06	8,89	1,17
NaCl	0,00	10,05	9,36	0,69
	0,029	10,05	9,55	0,50
	0,145	10,05	9,90	0,15
	0,290	10,05	10,05	0,00
NaBr	0,00	9,99	9,28	0,71
	0,0009	9,99	9,40	0,59
	0,0018	9,99	9,45	0,54
	0,0044	9,99	9,58	0,41
	0,0090	9,99	9,65	0,34
	0,0180	9,99	9,75	0,24
	0,0600	9,99	9,90	0,09
NaJ	0,00	9,99	9,27	0,72
	0,0011	9,99	9,82	0,17
	0,0035	9,99	9,96	0,03

On summarizing the results the studied ions can be divided into two groups regarding their effect:

I. The induced error is increased by: Cu(II), Ag(I), Be(II), Zn(II), Cd(II), Hg(II), Fe(III) ions. From among anions fluoride has an error increasing effect.

II. The induced error is decreased by: Na, K, Mg, Ca, Sr, Na, Sn(IV), Pb(II), Bi(III), Cr(III), Ce(III), Al(III), Tl(III), Co(II), Ni(II) ions. From among anions metasilicate, phosphate, arsenate, sulphate, selenate, molybdenate, tungstate, borate and ferricyanide also decrease the error.

Ammonium, uranyl, manganese(II) ions exert a strong error-decreasing effect similarly as from among anions chloride, bromide, iodide and acetate ions do.

Interpretation of the above described effects will be found elsewhere [3].

* * *

Thanks are due to Prof. Dr. Z. G. SZABÓ for his kind interest in this work.

ИНДУКЦИОННЫЕ РЕАКЦИИ СРЕДИ ПЕРОКСИ-СОЕДИНЕНИЙ. II

Действие посторонних веществ на реакцию в системе H_2O_2—$H_2S_2O_8$—$KMnO_4$

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Действие посторонних ионов на индукционную реакцию в системе

$$H_2O_2—H_2S_2O_8—KMnO_4\ [—Ce(SO_4)_2]$$

было изучено и установлено что индукционная ошибка увеличивается под воздействием ионов серебра (I), меди (II), железа (III), и она уменьшается под эффектом ионов щелочи, щелочноземельных металлов, олова (IV), свинца (II), хрома (III), никеля (II) кобальта (II), церия (III), молибдата (VI), и вольфрамата (VI), и очень значительно галоидных ионов.

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